Quenching of Intramolecular Exciplexes by Pyridine and Methylpyridines Suggesting Triple Exciplex (D′DA)* Formation

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Abstract: Intramolecular exciplex (DA)* fluorescence of 1-(9,10-dicyano-2-anthryl)-3-(1- or 2-naphthyl)propane was quenched by pyridine and methylpyridines (D′). Double exponential decay of the intramolecular exciplex was observed at room temperature, while a single exponential decay of the exciplex in the 9,10-dicyanoanthracene and naphthalene system was observed. The result in the former system implies the formation of a new type of triple exciplex, (D′DA)*, including pyridine molecule, though neither new fluorescence nor transient absorption spectrum due to the triple exciplex was detected. Association and dissociation rate constants of (D′DA)* obtained in the intramolecular system decrease in the following order of the quenchers: pyridine > 4-methyl- > 3,5-dimethyl- > 2-methyl- > 2,6-dimethylpyridine. These results suggest that the nonbonding orbital of a nitrogen atom in a pyridine ring may play an important role in the *ter*electronic interaction, (D′DA)*, in the excited state.

Since Beens and Weller[1] reported the triple complex formation in the excited state (triple exciplex) between 1,4-dicyanobenzene and two naphthalene molecules, some of the investigations on the triple exciplex were reported.[2,3] Grellmann and Suckow[3] reported the triple exciplex formation in the anthracene and *N,N*-diethylaniline system, and discussed the ionization and intersystem crossing leading to the formation of the triplet state of anthracene. Mimura and Itoh[4-6] demonstrated the formation and reversible dissociation of the triple exciplex $(D_2A)^*$ in the system of 1,4-dicyanobenzene and alkylnaphthalenes by double exponential decay of the exciplex (DA)*, and also reported an intramolecular triple exciplex formation between two naphthyl moieties of 1,3-dinaphthylpropane and 1,4-dicyanobenzene. The sequence of the electron donor and acceptor, (DDA)*, and the electronic structure in the triple exciplex were shown by experimental and theoretical points of view. On the other hand, Caldwell et al. reported the exciplex quenching suggesting the *ter*molecular interaction between the exciplex and the second electron donor or acceptor.

This paper[8] describes the fluorescence quenching of the intramolecular exciplex in 1-(9,10-dicyano-2-anthryl)-3-(1- or 2-naphthyl)propane[9] by pyridine and alkylpyridines in comparison with that of the intermolecular system of 9,10-dicyanoanthracene (DCA) and naphthalene.[10] Double exponential decay of the intramolecular exciplex (DA)* was observed in the quenching by pyridine and methylpyridines (D′), while only single exponential decay of the exciplex was observed in the DCA–naphthalene systems. The result of the intramolecular exciplex quenching suggests the formation and dissociation of a metastable triple exciplex, (D′DA)*, including pyridine or methylpyridine molecule (D′), though neither new fluorescence nor a transient absorption spectrum due to (D′DA)* is observed. The obtained association rate constants of the triple exciplex are much smaller in the quenching by 2-methyl- and 2,6-dimethylpyridines than by 4-methyl- and 3,5-dimethylpyridines. The triple exciplex formation seems to be hindered by 2- and 6-methyl groups, and the nonbonding orbital of the pyridine nitrogen atom seems to play an important role in the (D′DA)* formation, though the structure is obscure at this stage.

Experimental Section

Samples and solvents were purified by the methods described in the previous papers.[9,10] Pyridine and methylpyridines (Nakarai GR grade) were purified by distillation after refluxing with potassium metal for 5 h. The solutions of samples contained in a rectangular quartz cell (1 cm) with graded seals were purged by dry nitrogen gas or degassed by freeze–pump–thaw cycles. Both methods afford the same experimental results. All absorption and fluorescence spectra were recorded on Hitachi 323 and MPF-4 spectrophotometers at room temperature, respectively. The fluorescence decays and the time-resolved fluorescence spectra were determined by analyzing exponential decay curves measured by an oscilloscope (Tektronix 465) and a photomultiplier (HTV R666) and by an excitation with a coaxial N_2 gas laser which has a maximum ~20 kW photon peak intensity at 337 nm and 4–5-nsec duration. Observed fluorescence decay curves were analyzed by a computer-simulated deconvolution.[11]

Results and Discussion

The tetrahydrofuran (THF) solution of 1-(9,10-dicyano-2-anthryl)-3-(1- or 2-naphthyl)propane (β,α- or β,β-DCAN) exhibits intramolecular exciplex fluorescence in the 500–580-nm region at room temperature, as reported previously.[6] Figure 1 shows the fluorescence spectra of THF solutions of β,β-DCAN containing several concentrations of pyridine at room temperature (20–23 °C). The exciplex fluorescence at 500–580 nm as well as 9,10-dicyanoanthryl (DCA) moiety fluorescence at 400–450 nm was remarkably quenched by pyridine. However, the exciplex and also DCA moiety fluorescence were much less quenched by 2,6-dimethylpyridine in THF, as shown in Figure 2. In the fluorescence quenching of the exciplex, there seem to be several mechanisms such as a complex formation both in the ground and excited states, photoionization, energy transfer, and so on. Pac and Sakurai reported the dynamic quenching of exciplexes in 2-naphthonitrile-2-methylfuran and -2,3-dimethylbut-2-ene systems by pyridine.[12] The electronic absorption spectra of a THF solution exhibit no complex formation between β,β-DCAN (also β,α-DCAN) and pyridine molecule in the ground state. In the intramolecular exciplex quenching by pyridine (several methylpyridines) reported here, the photochemical scheme (Scheme I) involving the formation of a new type of triple exciplex (D′DA)* is tentatively assumed,[3,5] where A = 9,10-dicyanoanthryl and D = naphthyl moieties and D′ = quencher. The quenching ratio of (I_E'/I_E) of the exciplex fluorescence by the quencher is expressed by the equation

$$I_E'/I_E = (I_E^0/I_E)(I_A/I_A^0) = 1 + pk_7\tau_E^0[D'] \quad (1)$$

$$= 1 + \{(k_9 + k_{10})k_7[D']/(k_4 + k_5 + k_6)(k_8 + k_9 + k_{10})\}$$

$$p = (k_9 + k_{10})/(k_8 + k_9 + k_{10}),\ \tau_E^0 = (k_4 + k_5 + k_6)^{-1}$$

where I^0 and I are fluorescence intensities in the absence and

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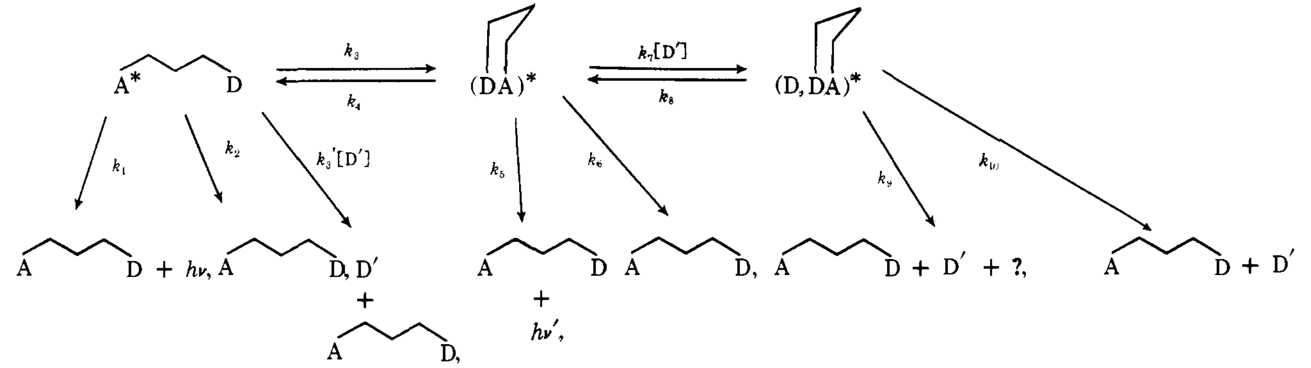
Scheme I



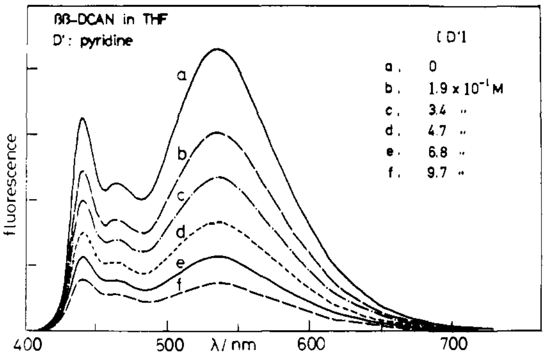


Figure 1. Fluorescence quenching of the THF solution of β,β-DCAN (2.8×10^{-6} M) by pyridine at room temperature (excitation wavelength, 380 nm).

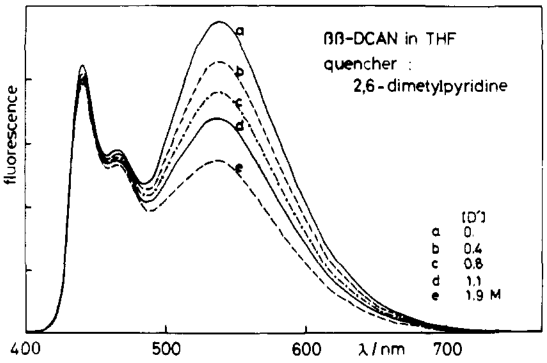


Figure 2. Fluorescence quenching of the THF solution of β,β-DCAN (2.5×10^{-6} M) by 2,6-dimethylpyridine at room temperature (excitation wavelength, 380 nm).

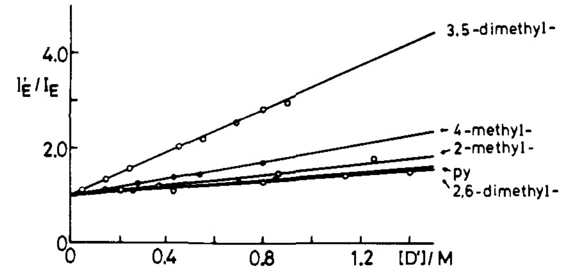


Figure 3. Stern-Volmer plots (I_E'/I_E) of the exciplex quenching of β,β-DCAN (3×10^{-6} M) by pyridine and several methylpyridines. Fluorescence intensity (I_E) was monitored at 650 nm.

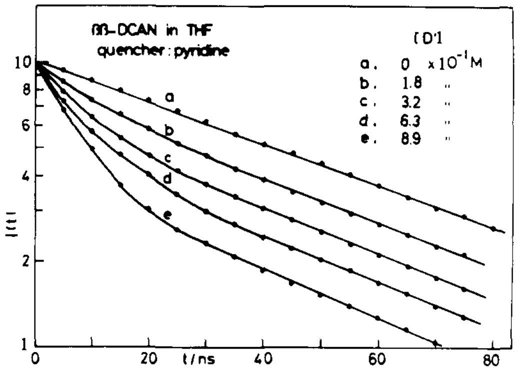


Figure 4. Fluorescence decay curves of the β,β-DCAN exciplex (monitored at 600 nm) in THF solutions containing several concentrations of pyridine (β,β-DCAN, 3.0×10^{-6} M). The time indicated in an abscissa is after a peak of signal of which intensity was normalized at 0 ns, since a very short rise time ($< \sim 1$ ns) of the exciplex fluorescence was observed, as mentioned in the text.

presence of D′, respectively; subscripts E and A represent the exciplex and DCA (moiety) fluorescence, respectively. Here, if the formation of a metastable excited-state complex (D′A)* between DCA moiety and pyridine (D′) is assumed in the reaction scheme, the formation of a different type of triple exciplex (D′AD)* by an intramolecular interaction in DCAN might be taken into account. However, this reaction path was neglected here. It is because the fluorescence quenching experiments of 9,10-dicyanoanthracene by pyridine (methylpyridines) in THF suggest no excited-state complex (D′A)* formation.[13]

Linear plots of $(I_E^0/I_E)(I_A/I_A^0)$ vs. [D′] were obtained in the exciplex quenching of the DCAN system by several quenchers (pyridine and 2-methyl-, 4-methyl-, 2,6-dimethyl-, and 3,5-dimethylpyridines), as shown in Figure 3. The quenching effect of the exciplex and also DCA moiety fluorescence were observed to be much smaller by 2,6-dimethylpyridine than by 3,5-dimethylpyridine. On the other hand, fluorescence decay curves of the intramolecular exciplex (DA)* in THF solutions containing several concentrations of pyridine were determined at room temperature. As shown in Figure 4, a short component decay curve appears at a concentration of D′ more than 0.1 M in the THF solution. However, this double exponential decay curve might be due to the superimposed decay of the DCA moiety fluorescence on that of the exciplex. Time-resolved fluorescence spectra exhibit the same fluorescence maxima independent of the time delayed after a laser pulse, and also independent of the concentration of the quencher. Further, intensity ratios of the long-lived and short-lived components of the exciplex fluorescence are constant in the wavelength region longer than 580 nm, as shown in Figure 5. Then the facts imply the real double exponential decay of the exciplex (DA)*.

Time-dependent concentration of (DA)* is expressed by the following well-known equation in the reaction scheme mentioned above:[3]

Table I. Decay Parameters of the Fluorescence Quenching of Intramolecular Exciplexes

exciplex	β,β-DCAN					β,α-DCAN
quencher[a]	py	4-MP	3,5-DMP	2-MP	2,6-DMP	py
$(k_4 + k_5 + k_6)/10^7\ M^{-1}\ s^{-1}$	1.6	1.6	1.6	1.6	1.6	1.3
$k_7{}^d/10^7\ M^{-1}\ s^{-1}$	26	19	16	5.7	$(1.0)^b$	22
$k_8{}^d/10^7\ s^{-1}$	15^e	10	5.9	5.9	$(4.0)^c$	8.2
$(k_9 + k_{10})^d/10^7\ s^{-1}$	0.41^e	0.8^e	1.7	1.1	$(6.0)^c$	0.21
$pk_7\tau_E{}^0/M^{-1}$	0.43	0.91	2.3	0.55	0.39	0.55
$k_3'\tau_A{}^0/M^{-1}$	3.0	3.4	3.7	0.79	0.041	2.1

[a] py = pyridine, 4-MP = 4-methylpyridine, 3,5-DMP = 3,5-dimethylpyridine, 2-MP = 2-methylpyridine, and 2,6-DMP = 2,6-dimethylpyridine. [b] Since the rate constants, k_7, of 3,5-DMP and 2-MP are similar to the exciplex quenching constants, k_q, of DCA-naphthalene (Table II), respectively, k_7 of 2,6-DMP was roughly assumed from k_q of 2,6-DMP. [c] Estimated from assumed k_7 and $pk_7\tau_E{}^0$. [d] Errors are approximately ±15%. [e] Refined from data reported in ref 8.

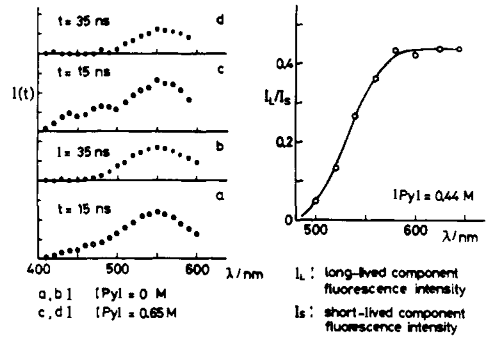


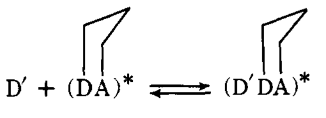
Figure 5. Time-resolved fluorescence spectra of THF solutions of β,β-DCAN (3.0×10^{-6} M), and intensity ratios (I_L/I_S) of the long-lived and short-lived components of decay in the exciplex fluorescence. Time indicated in the time-resolved spectra is after a peak of a laser pulse; I_L and I_S were determined from decay curves of each wavelength.

$$[(DA)^*] = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t) \quad (2)$$

$$\lambda_{1,2} = \frac{1}{2}[k_4 + k_5 + k_6 + k_7[D'] + k_8 + k_9 + k_{10} \mp \{(k_8 + k_9 + k_{10} - k_4 - k_5 - k_6 - k_7[D'])^2 + 4k_7k_8[D']\}^{1/2}]$$

$$\lambda_1 + \lambda_2 = k_4 + k_5 + k_6 + k_7[D'] + k_8 + k_9 + k_{10} \quad (3)$$

where the pumping function of (DA)* was assumed to be almost identical with that of a laser pulse because of a short lifetime of A* and of a short rise time of (DA)* fluorescence. A computer-simulated deconvolution of the double exponential decay of the exciplex (DA)* fluorescence affords time constants λ_1 and λ_2 in several concentrations of pyridine. Typical two-component decay of the intramolecular exciplex fluorescence was also observed in the quenching by 2- and 4-methyl- and 3,5-dimethylpyridines. Figure 6 shows linear plots of ($\lambda_1 + \lambda_2$) vs. [D'] yielding k_7 and ($k_8 + k_9 + k_{10}$). From eq 1 and 3, the rate constants k_7, k_8, and ($k_9 + k_{10}$) were obtained, as summarized in Table I. These results of the quenching of the intramolecular exciplex suggest the formation and dissociation of a metastable triple exciplex, (D'DA)*, including the respective methylpyridine (eq 4), though neither new fluorescence nor transient absorption due to (D'DA)* is observed at this stage.



$$D' + (DA)^* \rightleftarrows (D'DA)^* \quad (4)$$

The exciplex as well as DCA moiety fluorescence was much less quenched by 2,6-dimethylpyridine than by 3,5-dimethylpyridine. Since no double exponential decay of the (DA)* fluorescence was observed in the quenching by 2,6-dimethylpyridine, association and dissociation rate constants of (D'DA)* cannot be evaluated by the same method as described above. Therefore, assuming k_7 from the quenching constant of (DA)* of DCA-naphthalene, as will be mentioned later, several rate constants were tentatively estimated from $pk_7\tau_E{}^0$ and k_7, as summarized in Table I. The association and dissociation rate constants (k_7 and k_8) of the intramolecular exciplex and several methylpyridines decrease in the following order: pyridine > 4-methyl- > 3,5-dimethyl- > 2-methyl- > 2,6-dimethylpyridines. Further, the ratio of association and dissociation rate constants (k_7/k_8) also decreases in almost the same order. This implies that the dissociation process of (D'DA)* to (DA)* is more significant in 2,6-dimethylpyridine than in 3,5-dimethylpyridine. In this exciplex quenching, a single exponential decay of (DA)* is apparently observed on condition that ($k_8 + k_9 + k_{10}$) is much greater (or smaller) than ($k_4 + k_5 + k_6 + k_7$ [D']), and that the longer lifetime component is much greater (or smaller) than the short-lifetime component, i.e., $c_1 \gg c_2$ (or $c_1 \ll c_2$) in eq 2. These arguments seem to be well consistent with the observation of the single exponential decay of (DA)* in the quenching by 2,6-dimethylpyridine within observable limitation of our experimental setup.

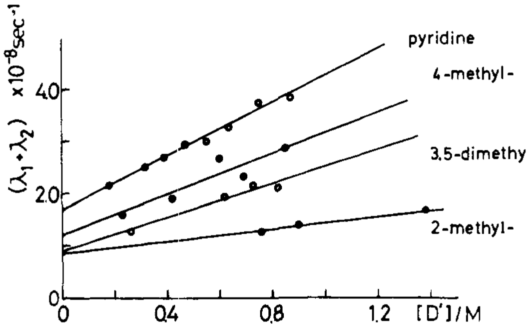


Figure 6. Plots of ($\lambda_1 + \lambda_2$) vs. concentrations [D'] of pyridine and several methylpyridines. Concentrations of β,β-DCAN in THF are 2-3 $\times 10^{-6}$ M.

The first ionization potentials from the nonbonding orbital and from the π orbital of the pyridine ring are very close to each other.[14,15] Further, 2,6- and 3,5-dimethylpyridines have similar ionization potentials and almost the same electronic structure. However, the quenching properties of these two dimethylpyridines shows significant differences. A similar difference of rate constants (k_7 and k_8) was also observed between 2- and 4-methylpyridines. The fact can be attributable neither to the ionization potential of the nonbonding orbital nor to that of the π orbital, but to the steric factor of the methyl group at the 2 and 6 positions.

The intermolecular exciplex fluorescence in the DCA and naphthalene system was quenched by pyridine and other methylpyridines more efficiently than the DCA fluorescence, as shown in Figure 7. The exciplex fluorescence of these sys-

Table II. Ionization Potentials of Quenchers and Fluorescence Decay Parameters of the DCA-Naphthalene System in THF at Room Temperature

quenchers[a]	py	4-MP	3,5-DMP	2-MP	2,6-DMP
$I_p(n)/eV^b$	9.60	9.50	9.52	9.50	9.30
$I_p(\pi)/eV^c$	9.75	9.60	9.25	9.20	8.90
$k_{3'}{}^{d}/10^7\ M^{-1}\ s^{-1}$	9.2	11	11	4.0	1.0
$k_q{}^{d}/10^7\ M^{-1}\ s^{-1}$	6.4	8.4	15	2.3	1.3

[a] Abbreviations of quenchers are shown in Table I. [b] Ionization potentials of nonbonding orbital of pyridine ring. See ref 14 and 15. [c] Ionization potentials of π orbitals of pyridine ring. See ref 14 and 15. [d] Errors of rate constants are approximately ±10%.

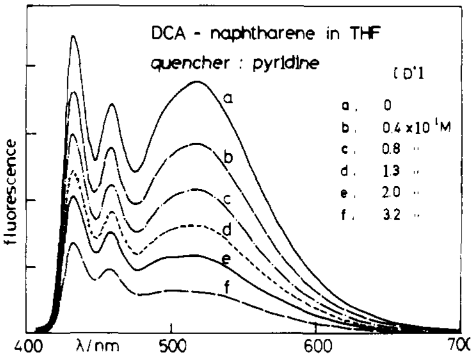


Figure 7. Fluorescence spectra of the THF solutions of DCA (2.6×10^{-6} M) and naphthalene (1.0×10^{-6} M) quenched by several concentrations of pyridine at room temperature (excitation wavelength, 380 nm).

tems exhibits only single exponential decay and the decay constant increases with increasing concentration of D'.[16] Stern-Volmer plots of the fluorescence intensity expressed approximately by the following equation are shown in Figure 8.

$$I_E'/I_E = (I_E^0/I_E)(I_A/I_A^0) = 1 + k_q\tau_E^0[D']$$

$$\tau_E = \text{fluorescence lifetime of (DA)*}$$

The quenching constant (k_q) of the intermolecular exciplex was determined to be $0.2\text{-}1.5 \times 10^8\ M^{-1}\ s^{-1}$, and much smaller in the quenching by 2-methyl- and 2,6-dimethylpyridines than that by 4-methyl- and 3,5-dimethylpyridines. The determined quenching constants (k_q) are summarized in Table II. The considerably small quenching constant of the intermolecular exciplex compared with that of the DCA fluorescence ($10^9\text{-}10^{10}\ M^{-1}\ s^{-1}$) seems to be attributable to the geometrical requirement in the *ter*molecular interaction[7] (an encounter interaction), though formation of the metastable triple exciplex (D'DA)* cannot be concluded in this intermolecular system.

The exciplex (DA)* should be quenched from the D side by D' (the quencher), i.e., D'···(DA)*. Such a geometry, proposed by Beens and Weller for the first time, was conclusively confirmed by the triple exciplex formation between 1,3-dinaphthylpropane and 1,4-dicyanobenzene,[4] and also by theoretical investigation of the triple exciplex formation.[6] If D and D' have the same or similar electronic structure, the sequence of the electron donor and acceptor should be (D'DA)*, though the interaction cannot be attributable only to the ionization potential of the quencher. If D' has a much smaller ionization potential than D, the exciplex (DA)* might be quenched from the A side by D', i.e., (DAD')*, which may lead to exciplex substitution[17] and/or photoionization.

$$(DA)^* + D' \rightarrow D + (AD')^*$$

In the exciplex quenching reported here, the ionization potential of the quencher is considerably larger than that of the electron donor in the exciplex (naphthyl or naphthalene). Then, the sequence of the *ter*electronic interaction seems to be (D'-DA)*. The quenching effect of methylpyridine was observed to depend remarkably on methyl substitution at the 2 and 6 positions, as mentioned above. Chandross and Thomas[18] and Taylor et al.[19] suggested the significant contribution of the nonbonding orbital of a nitrogen atom of an amine to the exciplex formation and/or fluorescence quenching in the naphthalene-alkylamine and aromatic hydrocarbon-*N,N*-dialkylaniline systems, respectively. The quenching behavior of methyl pyridine reported here suggests that the n orbital of the pyridine ring may play an important role in the fluorescence quenching, though the exact geometry of the *ter*electronic interaction and the role of the n orbital are not obvious at the present stage.

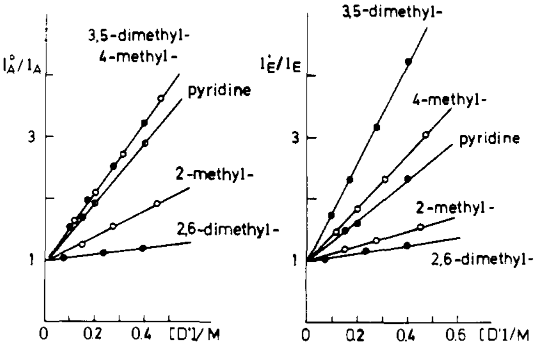


Figure 8. Stern-Volmer plots (left) of DCA fluorescence (2.6×10^{-6} M in THF) quenched by several quenchers, and plots (right) of the exciplex fluorescence of DCA (2.6×10^{-6} M) and naphthalene (6.0×10^{-1} M) quenched by several quenchers. Fluorescence intensities I_A and I_E were monitored at 434 and 620 nm, respectively.

The dissociation rate constant of the excimer was reported to be much lower in the intramolecular system than in the corresponding intermolecular system. Zachariasse[20] reported that the association rate constant of the excimer in 1,3-di(biphenyl)propane is approximately 10^3 greater than the dissociation rate constant. The association and dissociation behavior in the intramolecular exciplex may be similar to that in the excimer. Apparently, this is due to the effect of the trimethylene chain that locks the molecule in the excimer (DD)* or exciplex (DA)* state. Here, the intramolecular exciplex and quencher come together to form the nonfluorescent triple exciplex, (D'DA)*, which may dissociate simultaneously to (DA)* and D', as mentioned above (eq 5). In the intermolecular system of DCA and naphthalene, however, only single exponential decay of the exciplex means that the dissociation process of (D'DA)* to (DA)*, if an encounter complex (D'···DA)* is formed, is not significant. Then it is likely that the triple exciplex in the DCA-naphthalene-pyridine system dissociates into component molecules.

$$D' + (DA)^* \rightleftharpoons (D' \cdots DA)^* \rightleftharpoons (D'DA)^* \qquad (5)$$

Acknowledgment. The authors wish to acknowledge the financial support of the Grant-in-Aid (221611) of the Ministry of Education of Japan (Laser Spectroscopy).

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(13) Furthermore, if (DA)* is formed from (D′AD)* in the intramolecular system of DCAN, linear plots of $(I_e^0/I_E)(I_A/I_A^0)$ vs. [D′] cannot be observed, as will be mentioned later.
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(16) If the same reaction scheme as mentioned in the intramolecular system is assumed also in the intermolecular exciplex quenching of DCA–naphthalene, and if $(k_4 + k_5 + k_6 + k_7[D'])$ is much greater than $(k_8 + k_9 + k_{10})$, almost single exponential decay curves may be obtained, as mentioned above. In the practical case of $k_7[D'] \gg k_8$, the quenching constant, k_q, of DCA–naphthalene exciplex becomes approximately identical with k_7 in the reaction scheme mentioned above.
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Hydrocarbon Analogues of the Type II Photoeliminations of Ketones. Photochemistry of 1-Substituted 4-Phenyl-4-pentenes[1]

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Received September 19, 1978

Abstract: Direct irradiation of 1,4-diphenyl-4-penten-1-ol produces mainly 2-methyl-2,5-diphenyltetrahydrofuran, while benzophenone-sensitized photolysis gives α-methylstyrene, acetophenone, and 1,4-diphenyl-1-pentanone. The direct irradiation is postulated to proceed via the radical anion of the alkene. A mechanism for the inefficient triplet state reaction ($\Phi = 0.0005$) is proposed which involves initial hydrogen abstraction by the methylene carbon of the excited alkene to give a 1,4 biradical, which then produces the observed products. The mechanism is analogous to the accepted mechanism for the type II photofragmentation of ketones. The mechanism is supported by solvent effects and deuterium-labeling studies. Two related alkenes, 4-phenyl-4-penten-1-ol and 1,4-diphenyl-4-pentene, show similar photochemical behavior, although they react even less efficiently than 1,4-diphenyl-4-penten-1-ol.

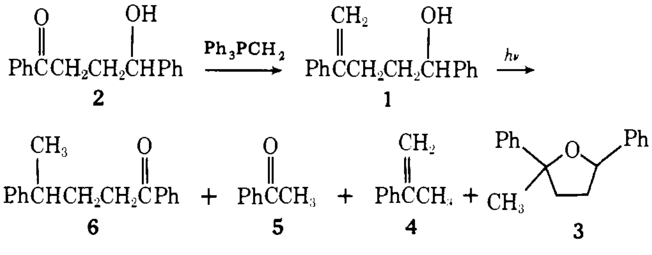
There are now a number of reports in the literature describing the photoinduced abstraction of hydrogen atoms by carbon which occurs in various molecules containing carbon–carbon double or triple bonds. Some examples include intermolecular abstractions by acyclic alkenes,[2-4] cyclic alkenes,[5,6] α,β-unsaturated ketones,[7,8] α,β-unsaturated esters,[9] and acetylenes.[10] Intramolecular abstractions by alkenes,[1,11-17] α,β-unsaturated enones,[18] and α,β-unsaturated amides[19] have also been observed. We report here the full details of our study of the photochemistry of substituted phenylpentenes. These compounds undergo intramolecular hydrogen abstractions very similar to the type II reaction of ketones,[20] although much less efficiently.

Results

For our initial studies we chose to investigate the photochemistry of 1,4-diphenyl-4-penten-1-ol (**1**), for two reasons. Based on the reported substituent effects on the type II reaction of ketones,[20a] we felt that both the phenyl and hydroxyl groups on carbon 1 would increase the rate of hydrogen abstraction. In addition, if **1** were to undergo a type II reaction, the 1,4 biradical which would result could also be generated by irradiation of 1,4-diphenyl-1-pentanone (**6**), and thus an independent check on the behavior of this biradical would be available.

The synthesis of **1** was readily accomplished by a Wittig reaction of 1,4-diphenyl-4-hydroxy-1-butanone[21] (**2**), with excess methylenetriphenylphosphorane. The photochemistry of **1** depended on both the solvent employed and the multiplicity of the excited state. The photoproducts observed under various conditions are summarized in Table I.

The major product from the direct irradiation of **1** in either hexane or benzene was 2-methyl-2,5-diphenyltetrahydrofuran (**3**), obtained as a mixture of stereoisomers. In addition, small amounts of α-methylstyrene (**4**), acetophenone (**5**), and an unidentified photoproduct were formed. Photoproduct **3** was identified by comparison of its spectral properties with those of an authentic sample prepared by acid-catalyzed cyclization of **1**. Direct irradiation of **1** in *tert*-butyl alcohol gave the same products, although the relative percentages changed. The ef-



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